TRANSFORMATION OF RIVERINE ORGANIC MATTER IN ESTUARIES

John R. Ertel[1], James J. Alberts[2] and Mary T. Price[2]

AUTHORS: [1]Department of Geology and Marine Science Program, GGS Building, The University of Georgia, Athens, Georgia 30602; and [2]The University of Georgia Marine Institute, Sapelo Island, Georgia 31327.
REFERENCE: Proceedings of the 1991 Georgia Water Resources Conference, held March 19 and 20, 1991, at The University of Georgia, Kathryn J. Hatcher, Editor, Institute of Natural Resources, The University of Georgia, Athens, Georgia.

ABSTRACT

Laboratory mixing experiments were performed using water from nine Southeastern US rivers and seawater to determine the physical/chemical processes occurring to riverine organic matter when in contact with salt water. The dominant salt-induced changes that occur to riverine organic components were consistent increases in the particulate organic carbon concentrations (POC) and decreases in the dissolved organic carbon (DOC) concentrations. DOC to POC transformations occurred both in the presence and absence of the natural riverine particles, suggesting that both flocculation and adsorption of riverine DOC occur in salt water. These transformations from DOC to POC begin at low salinities (5 ppt.) and continue to increase to 20 ppt., indicating that these processes occur throughout the salinity range normally found in estuaries.

INTRODUCTION

Rivers carry vast amounts of natural and anthropogenic organic compounds to the coastal marine environment. The biological impact and ultimate geochemical fate of these terrestrially-derived compounds in the oceans are both highly dependent on the physical state of the organic matter in seawater, that is, whether these riverine components become part of the marine dissolved (DOC) or particulate (POC) organic carbon pools. The interfaces between land and ocean, estuaries and salt marshes, are highly dynamic zones, where physical, chemical and biological processes can cause major alterations in the riverine carbon fluxes. Thus, the distributions and forms of organic matter measured in fresh water might be unrepresentative of the physical state of this material in seawater.

We are currently investigating the transformations that might occur between riverine DOC and POC in estuaries due to one of the major physical processes: changes in salinity as river water mixes with seawater. Transformations of organic matter in the presence of salt could include adsorption, flocculation and desorption and thus could result in either net increases or decreases in the predicted DOC and POC fluxes. Our approach is to conduct laboratory mixing experiments with different sources and types of river water and seawater and to determine the changes in DOC and POC concentrations at increasing salinities. In addition, we are examining the elemental and molecular characteristics of that portion of DOC that is converted to POC. These results will permit a better estimate of the contribution of organic carbon and nitrogen and specific terrestrial biomarkers to the ocean.

METHODS

Water was collected upstream of any tidal influence from nine rivers in the Southeast USA in March of 1989 and from the Altamaha and St. Marys Rivers in January of 1990. Samples were from the Pee Dee (PD), Black (BL), Edisto (ED), Savannah (SAV), Ogeechee (OG), Altamaha (ALT), Satilla (SAT), St Marys (SM) and Suwannee (SUW) Rivers. Seawater was collected at the shelfbreak of the Georgia Bight. Portions of the river water and all seawater were filtered through 0.45 um glass fiber filters prior to the mixing experiments.

Two sets of experiments were performed. The first set of experiments was designed to determine the changes in concentrations of riverine DOC and POC for a wide variety of river water types when mixed with equal portions of seawater and also the effect that naturally present river particles would have on salt-induced DOC-POC transformations. Thus, both filtered and unfiltered river water from the nine Southeast rivers were mixed with filtered seawater to a resulting salinity of 15 ppt. The second experiment was designed to ascertain the salinity range over which these transformations were important. In the second experiment filtered and unfiltered water from the Altamaha and St Marys Rivers were mixed with filtered seawater to final salinities ranging from 5 to 20 ppt.

All samples were shaken for 24 hours and then filtered through pre-ashed glass fiber filters to determine the resulting POC concentrations (by CHN analyses).

The filtrate were stored for DOC analysis. POC and DOC analyses were performed using a Perkin-Elmer 2400 Elemental Analyzer and an Ionic 555 Carbon Analyzer, respectively.

All results discussed below are expressed as changes relative to the amount of POC or DOC that is present in the river water portion of that mixture, that is, results are normalized to the amount of river water. Since the seawater was filtered prior to the mixing experiments, it contained no POC, but had DOC concentrations of 2 ppt. Mass balance calculations indicate that all the marine and riverine organic matter could be accounted for by the measured DOC and POC concentrations.

RESULTS AND DISCUSSION

In all of the mixing experiments conducted as part of this project, there were significant increases in the POC concentrations and measurable decreases in DOC concentrations in the river waters after the addition of seawater. These results indicate that the dominant transformation which occurs to riverine organic matter due to increasing salinity is the formation of POC from DOC. No evidence suggests that POC is being released from the riverine particles to form DOC. These results confirm previous laboratory and field studies which indicate that a portion of the riverine DOC is removed from solution in seawater (Sholkovitz, 1976; Sholkovitz and Copland, 1981). Because Southeast rivers generally have 10 times higher concentrations of DOC than POC (Alberts et al., 1990), these POC to DOC transformations will greatly affect the estimates of riverine POC inputs to the ocean, but will affect the DOC fluxes calculated from freshwater measurements only slightly.

Effect of river particles

In the first set of experiments, the increase in POC concentrations after the addition of filtered seawater for all 9 rivers ranged from .2 to 2.5 mg C/l, which represents 35 to 260% of the POC values measured in freshwater (Fig. 1). The DOC concentrations for these rivers ranged from 10 to 40 mg C/l and thus, from 1 to 12% of the riverine DOC was converted to POC due to the salinity change. Previous studies had indicated the DOC is conservative in estuaries (Mantoura and Woodward, 1983), although loss of less than 5% of the DOC is within experimental error of field measurements and would not be detected.

The rivers chosen for this mixing experiment contained a wide range of POC and DOC concentrations as measured in freshwater. Most rivers showed greater than 100% increase in POC concentrations after mixing with seawater, indicating that these

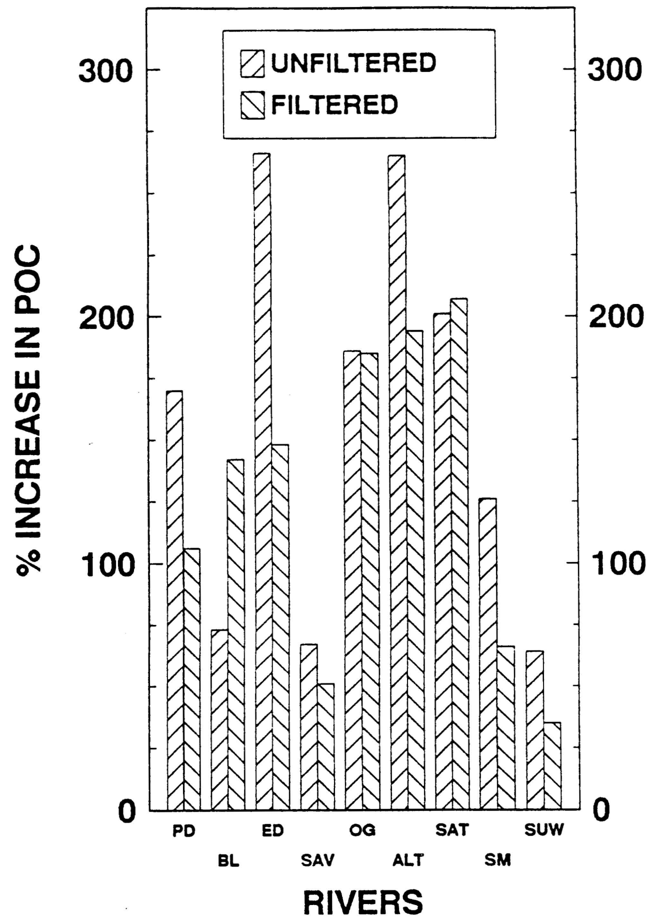

Figure 1. Percent increase in POC concentrations in river water after mixing with seawater. Unfiltered samples were corrected for the POC added with the river water.

transformations occur over a variety of natural conditions. Similar large increases were seen for the particulate organic nitrogen (PON) concentrations.

The average C/N ratio for particles collected after mixing with seawater was 18, which is higher than the C/N ratio for the particulate organic matter collected upstream of seawater influence, which averages about 15 (Alberts et al., 1990). These results indicate that there is not only a significantly greater riverine POC and PON flux to the ocean than is measured in freshwater but also that the particulate terrestrial organic matter entering the ocean is more carbon-rich than generally estimated for river particles (Meybeck, 1982). Thus, riverine POC in the ocean might be overall less nutritious to marine organisms and perhaps less likely to enter the marine food web.

For most of the rivers in this experiment, more DOC was removed upon addition of seawater when the natural riverine particles were left in solution (UNFILTERED, Fig. 1). Thus, particle surfaces appear to catalyze DOC to POC conversions. However, the fact that POC was also formed in river waters that had been filtered before mixing with seawater indicates that precipitation of organic matter is also occurring in addition to adsorption onto particle surfaces in the presence of salt. The average C/N ratio for the particles formed upon mixing in the filtered river water was slightly higher (22) than the average ratio calculated for the organic matter adsorbed onto the particles in the unfiltered samples (17). These results suggest that the salt-induced precipitation and adsorption removed different types of organic matter from water. We are currently investigating this question through the use of molecular biomarkers.

Effect of salt concentrations

In the second series of experiments, the relative amounts of DOC removed from solution (Fig. 2) and POC formed (Fig. 3) at 15 ppt. matched those of the previous mixing experiment for the Altamaha River. Similar results were also seen with the St Marys River, thus demonstrating that the salt-induced DOC to POC transformations are universal processes occurring to riverine DOC and are not dependent on characteristics of riverine organic matter found only during specific seasons.

The precipitation and adsorption of DOC began at low salinity (5 ppt.) and continued to increase to 15 to 20 ppt. The largest transformation from DOC to POC occurred over the salinity range of 5 to 10 ppt for both the filtered and unfiltered samples. The unfiltered samples consistently showed more POC formation

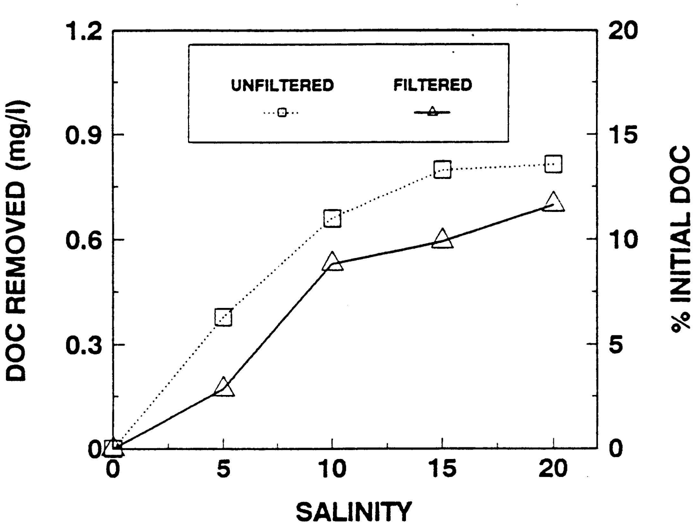

Figure 2. Changes in the riverine DOC concentration versus salinity for the Altamaha River mixing experiment. DOC values are corrected for DOC contributed by the seawater.

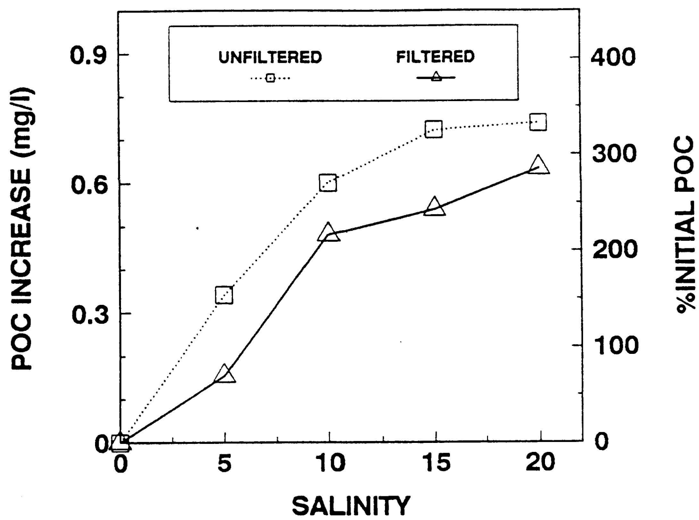

Figure 3. Increase in the POC concentration versus salinity for the Altamaha River mixing experiment. Unfiltered samples are corrected for the POC added with the river water.

(and DOC removal) than the filtered samples, indicating the importance of salt-induced adsorptive processes in addition to precipitation.

As seen in the profiles in Fig. 2 and 3, the effect of salt concentrations on these two processes appears to be different. For the unfiltered samples no further changes in DOC or POC concentrations occurred after 15 ppt. salinity. However, the POC concentration for the filtered samples continued to increase to 20 ppt. Thus, at 20 ppt. both filtered and unfiltered samples showed approximately the same degree of POC formation from DOC. These results suggest that the particles formed by precipitation of DOC in the filtered samples might act as adsorptive sites for more DOC, similar to the role of the natural riverine particles in the unfiltered samples.

As in the earlier experiment, the C/N ratios of the POC from the mixing experiments (13-15) were higher than the ratio for particles collected in freshwater (12). However, in this case no pattern was seen in the POC formed at different salinities.

SUMMARY

Mixing experiments have shown that riverine DOC is converted to POC due to changes in salinity that will be encountered in estuaries. Thus riverine POC and PON fluxes to the ocean measured in freshwater underestimate the concentration of riverine POC in the ocean by at least a factor of two. In addition, these mixing experiments strongly imply that DOC will not be conservative in estuaries, since for all rivers tested there was measurable conversion of DOC to POC.

Our results demonstrate that geochemical processes occurring in estuaries can significantly alter both the concentrations and compositions of riverine fluxes to the ocean and must be considered before any realistic assessment of carbon, nutrient or pollutant inputs to the marine environment from rivers can be made.

ACKNOWLEDGMENTS

We thank Amy Blanchard and Laura Case for their assistance in this project. This research is sponsored by the Georgia Sea Grant Program, supported by NOAA Office of Sea Grant, Department of Commerce, under grant NA84AA-D-00072.

LITERATURE CITED

Alberts, J.J., J.E. Ertel and L. Case. 1990. Characterization of organic matter in Rivers of the Southeastern United States. Verh. Int. Ver. Limnol. 24: 260-262.

Mantoura, R. F. and E. M. Woodward. 1983. Conservative behavior of riverine dissolved organic carbon in the Severn estuary: Chemical and geochemical implications. Geochim. Cosmochim. Acta 47: 1293-1309.

Meybeck, M. 1982. Carbon, nitrogen and phosphorus transport by world rivers. Am. J. Sci. 282:401-450.

Sholkovitz, E. R. 1976. Flocculation of dissolved organic and inorganic matter during mixing of river water and sea water. Geochim. Cosmochim. Acta 40: 834-845.

Sholkovitz, E. R. and D. Copland. 1981. The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in river water. Geochim. Cosmochim. Acta 45: 181-189.